

Title: Flexible organic electronic device and methods for preparing the same

The present invention relates to a flexible organic electronic device such as a display or a thin film transistor (TFT), and methods for preparing said device.

Displays are very thin screens that are widely used in machine vision systems such as portable computers and television sets. Such displays include light-emitting diodes (LEDs), organic light-emitting diodes (OLEDs), liquid crystal displays (LCDs) and field emission displays (FEDs). Displays are semiconductor devices that emit light under influence of an applied voltage. They generally comprise a substrate and an active layer, which is situated between a front electrode in the form of a transparent conductive layer and a back electrode layer. When an appropriate voltage is applied between the transparent conductive layer and the back electrode, light will be produced in the active layer, which light emits through the transparent conductive layer.

Thin film transistors (TFTs) are semiconductor devices which are used in electronic applications such as displays and electronic bar codes. They comprise a transparent conductive oxide layer that acts as gate electrode, a dielectric layer, a semiconductor layer, and a source and drain electrode. When an appropriate voltage is applied to the gate electrode, a conductive path is created between the source and the drain electrode, which makes electronic switching possible.

Conventional electronic devices as described above comprise inflexible substrates that are made of glass. Such substrates have the drawbacks that they are breakable and relatively heavy. In order to deal with these drawbacks flexible substrates have been developed that are cheaper, lighter and have increased ruggedness when compared to substrates that are made of glass.

In addition, it is observed that there exists the increasing desire to use organic active layers in electronic devices because such devices display improved properties in terms of processing, brightness, energy demand, and

compatibility with flexible applications when compared with conventional electronic devices.

Flexible electronic devices that comprise a polymeric substrate and an organic active layer have, however, the drawback that they can only be prepared at relatively low temperatures because the relative poor temperature stability of the polymeric materials of which the substrates are made to provide flexibility. Hence, high temperature deposition processes such as, for instance, Atmospheric Pressure Chemical Vapour Deposition (APCVD) cannot be applied to deposit a transparent conductive oxide layer onto the substrate. This is unfortunate because of the inherent nano-scale porosity of the layers prepared at low temperatures. Consequently, in most, if not all, flexible displays indium tin oxide (ITO) is used as the transparent conductive oxide because this material can suitably be deposited at a low temperature using Physical Vapour Deposition (PVD) processes. Reference can in this respect, for instance, be made to US 2002/0030770 A1 wherein a transparent electrode (ITO) is sputtered onto a substrate of glass on which substrate first a layer of polystyrene is coated as protection material for the electrode. The temperatures applied in such PVD processes are typically lower than 80 °C.

An additional problem with flexible organic electronic devices is that the device comprising an organic active layer needs to be protected against possible contact with water and oxygen, because these materials have a detrimental impact on the performance of the organic device. To provide such a protection presently a stack of several layers has to be provided additionally.

As regards the use of indium tin oxide it should be noted that it is a relatively expensive transparent conductive oxide and that the PVD processes used in connection with it are relatively slow and are operated at low pressure necessitating the need for expensive vacuum equipment. In addition, the performance of indium tin oxide, as far as the protection of the organic active layer is concerned, leaves considerable room for improvement.

Object of the present invention is to provide a flexible organic electronic device that has an improved long-term performance and is cheaper to make.

Surprisingly, it has now been found that flexible organic electronic devices with excellent long-term performance properties can be prepared when use is made of a removable substrate layer onto which a transparent conductive oxide layer can be applied at a high temperature, after which the removable substrate layer is removed at a later stage of the preparation process.

Accordingly, the present invention relates to a method for preparing a flexible organic electronic device comprising at least a first electrode comprising a transparent conductive oxide layer, an organic active layer, a second electrode and a polymeric substrate layer, whereby the transparent conductive layer is applied on a removable substrate layer or on one or more transparent layers previously applied onto the removable substrate layer at a temperature of at least 250°C, and the removable substrate layer is removed when the polymeric substrate layer has been applied.

The use of such a removable substrate layer allows the use of high temperature deposition processes, which makes it possible that cheaper transparent conductive oxides can be used and that the deposition processes can be carried out much faster. Additionally, it allows the formation of a transparent conductive oxide layer having improved properties to protect the polymeric substrate against water and oxygen, because it displays very low water and oxygen permeabilities.

Suitably, the method according to the present invention comprises the steps of:

- a) applying the first electrode, which comprises a transparent conductive oxide layer onto the removable substrate layer or on one or more transparent layers previously applied onto the removable substrate layer;
- b) applying the organic active layer onto the transparent conductive layer;

- c) applying the second electrode onto the organic active layer;
- d) applying the polymeric substrate layer onto the second electrode; and
- e) removing the removable substrate layer.

In another, and preferred, embodiment of the present invention the 5 method comprises the steps of:

- a) applying the first electrode, which comprises a transparent conductive oxide layer onto the removable substrate layer;
- b) applying one or more transparent layers onto the transparent conductive oxide layer.
- 10 c) applying the polymeric substrate layer onto the transparent conductive layer;
- d) removing the removable substrate layer;
- e) applying the organic active layer onto the transparent conductive layer on the side from which the removable substrate layer has been removed;
- 15 f) applying the second electrode onto the organic active layer; and
- g) applying a further polymeric substrate layer onto the second electrode.

This embodiment is preferred since the organic active layer will not be exposed to an etching process to remove the removable substrate layer.

The transparent conductive oxide layer can suitably be applied onto 20 the removable substrate layer by means of a deposition process such as Hot spraying, Atomic Layer Deposition (ALD), sol/gel deposition, Atmospheric Pressure Chemical Vapour Deposition (APCVD), Low Pressure Chemical Vapour Deposition (LPCVD) or a Plasma Enhanced Chemical Vapour Deposition (PECVD) process. The transparent conductive oxide layer is 25 preferably applied onto the removable substrate by means of an APCVD process. The transparent conductive oxide layer is suitably applied onto the removable substrate layer or one or more transparent layers previously applied onto the removable substrate layer at a temperature of at least 250°C, preferably at least 400°C, more preferably at a temperature in the range of 30 from 450 to 550°C, and most preferably in the range of from 490 to 530°C. The

application of such high temperatures allows the transparent conductive layer to obtain the desired properties.

The transparent conductive oxide layer may comprise one or more transparent conductive oxides selected from the group consisting of zinc oxide, 5 tin oxide, zinc stannate, and/or indium tin oxide. Preferably, the transparent conductive oxide layer comprises zinc oxide and/or tin oxide. More preferably, the transparent conductive oxide layer comprises tin oxide. The transparent conductive oxide can be doped with a material such as aluminium, fluorine, gallium or boron. Most preferably, the transparent conductive oxide layer 10 comprises tin oxide, which has been doped with fluorine. The thickness of the transparent conductive oxide layer can suitably be in the range of from 10 nm to 2000 nm, preferably in the range of from 450 nm to 850 nm.

The removable substrate layer can suitably be a foil of a metal or a metal alloy. Suitable metals include aluminium, titanium, copper, steel, iron, 15 nickel, silver, zinc, molybdenum, chromium and alloys thereof. Preferably aluminium, copper or iron is used or an alloy thereof. Most preferably, use is made of aluminium or an alloy thereof. The removable substrate layer can suitably have a thickness in the range of from 5 micron to 1 mm, preferably in the range of from 50 micrometer to 200 micrometer.

20 The removable substrate layer can suitably be removed by means of an etching process. Suitably, in such etching process use is made of an acid or a base such as nitric acid, sulphuric acid, sodium hydroxide (NaOH) or potassium hydroxide (KOH). When the removable substrate layer comprises a foil of aluminium preferably use is made of sodium hydroxide (NaOH) or potassium 25 hydroxide (KOH).

On the removable substrate layer one or more transparent layers may already have been applied, before the transparent conductive oxide layer is applied. Such transparent layers include layers comprising SiO_2 , SiO_{2-x} , Al_2O_3 , MgO , ZnO , ZrO_2 , TiO_2 , TiN , ZnS , SiO_xC_y , Si_3N_4 and/or SiO_xN_y . The polymeric 30 substrate layer may contain several layers that can suitably comprise one or

more polymeric materials selected from the group consisting of polyimids, polyamids, polyaramids, polyesters, polyolefins, liquid crystalline polymers (LCP), polycarbonates, polyacrylates, polymethacrylates, copolymers, blends of polymers and/or composites. The polymeric substrate layer may contain one or 5 more types of polymers, but in practice it will be preferred to use one particular type of polymer. Preferably, the polymeric substrate layer comprises polyesters and/or polyolefins. More preferably, the polymeric substrate layer comprises polyethyleneterephthalate (PET) or polyethylenenaphthalate (PEN). The polymeric substrate layer can suitably have a thickness in the range of 10 from 50 micrometers to 10 centimeters, preferably in the range of from 100 to 500 micrometer. The polymeric substrate layer can suitably applied to the second electrode layer and the transparent conductive layer by means of lamination.

The organic active layer can suitably comprise light emitting organic 15 molecules, one or more semiconducting polymers such as light emitting polymers, one or more conducting polymers and/or one or more semi-conducting polymers selected from the group consisting of polyanilines, polythiophenes, polypyroles, polyfluorenes, polyarylenes, polycabazoles, polyvinylcarbazoles, and derivatives, copolymers, and/or mixtures of these. The 20 organic active layer may contain one or more layers of the above named compounds, but in practice it will be preferred to use polyaniline or polyethylenedioxythiophene in one layer and the second organic active layer comprises the light-emitting polymer. The organic active layer can suitably have a thickness in the range of from 20 to 500 nm, preferably in the range of 25 from 50 to 150nm. The organic active layer can suitably be applied onto the transparent conductive oxide layer by means of spin coating or printing processes such as doctor blading, screenprinting or inkjet printing. The organic active layer is preferably applied onto the back electrode layer at a temperature below 100°C.

The second electrode may comprise a low work function material such as calcium, barium, lithium fluoride, magnesium covered with a layer of aluminium, silver or gold.

The second electrode can suitably have a thickness in the range of from 5 1 nm to 1 micrometer, preferably in the range from 1nm to 200nm. The second electrode can suitably be applied onto the organic active layer by means of sputtering or low-pressure vapour deposition or a printing process. The second electrode is preferably applied onto the organic active layer by means of a low-pressure vapour deposition process. The second electrode layer is preferably 10 applied onto the polymeric substrate layer at a temperature below 100 °C.

It will be appreciated by the skilled person that in displays the second electrode will comprise a back electrode, whereas in TFTs the second electrode will comprise both a source and drain electrode.

The transparent conductive oxide layer obtained in accordance with 15 the present invention constitutes a very effective carrier layer, which protects the active layer against water and oxygen. Depending on the particular use of the electronic device a further barrier layer may be applied on the transparent conductive oxide layer, before or after the removable substrate layer is removed in step e). Such further barrier layer may for instance comprise a 20 transparent oxide layer, a planomer containing layer or a transparent metallic layer. Various of these embodiments have been depicted in Figure 1.

The transparent oxide layer may for instance comprise SiO_2 , SiO_{2-x} , Al_2O_3 , ZnO , MgO , ZrO_2 , TiO_2 , TiN , ZnS , SiO_xC_y , Si_3N_4 and/or SiO_xN_y . The planomer is a nanocomposite consisting of a plate-like, non-permeable mineral and a 25 polymer matrix, whereby the plates are very thin, preferably between 1 and 10 nm and have an aspect ratio of at least 100. Preferably, such a mineral is formed from the mineral class of montmorillonites, hectorites, and saponites. The minerals exist preferentially in an exfoliated state within the polymer matrix material, i.e. the plates are separately dispersed. The matrix polymer 30 can be chosen out of known transparent barrier materials. The transparent

metallic layer may comprise Al, Ti, Cr, Ni, Ag or Mg. Such further barrier layer can suitably have a thickness in the range from 1nm to 5 μ m, preferably in the range of from 1 to 50 nm Alternatively, polymeric substrate layer is applied directly on the transparent conductive oxide layer before or after the 5 removable substrate layer has been removed in step e).

A polymeric substrate layer can be applied onto the further barrier layer to provide strength and flexibility. Such further polymeric substrate layer can suitably have a thickness in the range of from 1 μ m to 10 mm, preferably in the range of from 50 μ m to 1 mm.

10 As mentioned earlier, the flexible organic electronic devices according to the present invention can for instance be used in LCD-displays, thin film transistor technology, and organic light-emitting diodes (OLEDs). In a particular embodiment of the present invention the device comprises an organic light-emitting diode.

15 The flexible organic electronic devices obtained in accordance with the methods of the present invention display unique properties in terms of water and oxygen permeabilities.

Hence, the present invention also relates to a flexible organic electronic device obtainable by a method according to the present invention.

20 The present invention also relates to a flexible organic electronic device comprising at least a first electrode which comprises transparent conductive oxide layer, an organic active layer, a second electrode, and a polymeric substrate layer, wherein the transparent conductive oxide layer has very low water and oxygen permeabilities. Suitably, the transparent conductive oxide 25 layer displays a water permeability of less than 0.01g/m²/day, preferably less than 10⁻⁵ g/m²/day, whereas it displays an oxygen permeability of less than 10⁻¹ cc/m²/day, preferably less than 10⁻² cc/m²/day.

30 Another advantage of the flexible organic electronic device in accordance with the present invention is that by adjustment of the preparation conditions the transparent conductive oxide layer can obtain a surface

structure that allows emission of diffused light. This is attractive for applications in the field of displays.